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Metals in Ground Water: Sampling Artifacts and Reproducibility

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ABSTRACT

Field studies evaluated sampling procedures for determination of aqueous inorganic geochemistry and assessment of contaminant transport by colloidal mobility. Research at three different metal-contaminated sites has shown that 0.45 μm filtration has not removed potentially mobile colloids, when samples have been collected using low pumping flow rates (~ 0.2 - 0.3 L/min). However, when pumping velocities greatly exceed formation groundwater flow velocities, large differences between filtered and unfiltered samples are observed, and neither are representative of values obtained with the low flow-rate pumped samples. There was a strong inverse correlation between turbidity and representativeness of samples. Several different sampling devices were evaluated in wells (PVC) ranging in depths from 10 to 160 ft. Those devices which caused the least disturbance (i.e. turbidity) also produced the most reproducible samples irrespective of filtration. The following water quality indicators were monitored during well purging: dissolved O_2 , pH, Eh, temperature, specific conductance, and turbidity. Sampling was not initiated until all indicators had reached steady-state (usually ~ 2 to 3 casing volumes). In all cases turbidity was slowest to reach steady-state values, followed by dissolved oxygen and redox potential. Temperature, specific conductance, and pH results were generally insensitive to well purging variations.

INTRODUCTION

A primary ground-water sampling objective is the acquisition of representative elemental and molecular concentrations for the purpose of risk assessment at hazardous waste sites. These samples should include contaminants sorbed to naturally suspended inorganic and organic colloids, in addition to dissolved species. Particles with diameters less than 10 μm , referred to as colloids, may form in certain subsurface environments and be mobile at ground-water velocities.

Several studies have demonstrated contaminant transport by colloidal mobility (1,2,3,4). There is increasing concern that current methods of ground-water sample collection may exclude this component of the contaminant loading in a given system. If the purpose of sampling is to estimate total contaminant transport, substantial underestimations of contaminant mobility may result, due to its colloidal association. Numerous studies attest to the strong sorptive capabilities of secondary clay minerals; hydrous Fe, Al, and Mn oxides; and humic material of colloidal dimensions (5,6,7,8,9). If colloids as large as 0.45 - 3 μm are mobile, and capable of transporting contaminants large distances, then sampling protocols must make allowances for this component of transport. Likewise, transport models must incorporate this mechanism to provide better contaminant migration predictions.

If a secondary objective is accurate 'dissolved' inorganic concentrations, then samples should be filtered through 0.1 μm pore size filters or smaller in the field using in-line devices, and acidified immediately to $< \text{pH } 2$ with concentrated HNO_3 . Historically, 0.45 μm pore size filters have been used to differentiate between dissolved and particulate phases in water samples (10). If the intent of such

determinations is an evaluation of truly dissolved constituent concentrations, which would be important for geochemical modeling purposes, the inclusion of colloidal material less than $0.45\ \mu\text{m}$ will result in incorrect values (11,12,13,14). This is often observed with iron and aluminum where supposedly 'dissolved' values are thermodynamically improbable at their sample pH's. Conversely, if the purpose of sampling is to estimate 'mobile' contaminant species in solution, underestimations of mobility may result, due to colloidal facilitated transport by particles which are filtered out by $0.45\ \mu\text{m}$ filtration.

Disturbance of the subsurface environment is inevitable in the process of installing monitoring wells and collecting samples. Artifacts or contamination to samples can occur from the following: poor well construction; inadequate well development; corrosion, degradation, or leaching of well construction materials; improper well purging, sampling, processing, sample transportation and storage (15,16,17,18,19,20,21,22). Intuitively, it makes sense to minimize disturbance of the sampling zone to obtain representative and accurate data. Excessive turbidity is a common occurrence in samples, and can result from perturbation of sediments or entrained foreign particles. Natural turbidity may exist where conditions are favorable for the production of stable suspensions (e.g. low ionic strength waters, geochemical supersaturation, high clay content), whereas excessively rapid pumping or purging relative to local hydrogeological conditions is a frequent cause of artificial turbidity. Oxidation of anoxic or suboxic aquifer zones may result from high pumping rates which impact much larger segments of the aquifer than the interval of interest, causing the precipitation of iron oxyhydroxide and/or mixing of chemically distinct zones.

Sampling recommendations consistent with the above discussions and recommendations were summarized by Puls and Barcelona (23). Briefly these were the following:

- ♦ Isolation of the sampling zone with packers to minimize purge volume,
- ♦ Low flow rate pumping to minimize aeration and turbidity,
- ♦ Monitoring of water quality parameters while purging for establishment of baseline or steady-state conditions to initiate sampling,
- ♦ Maximize pump tubing thickness and minimize length to exclude atmospheric gases,
- ♦ Filtration for estimate of dissolved species and collection of unfiltered samples for estimates of contaminant mobility.

FIELD STUDY SITES

Between June, 1988 and February, 1991, three different field sites were used to address the above issues and to evaluate sampling techniques and recommendations. The first site studied is located at Pinal Creek, near Globe, Arizona, about 130 km east of Phoenix and about 170 km north of Tucson. The geology of the area has been described by Peterson (24). Copper has been mined since 1903 from granite porphyry adjacent to an aquifer at the site. A band of unconsolidated alluvium 300 to 800 m wide, as much as 50 m thick, and about 20 km long forms the upper, central part of the aquifer in a valley along Miami Wash and Pinal Creek. Most of the sediment in the alluvium ranges in size from fine sand to coarse gravel, but clay and boulder lenses also are present. Alluvial basin fill more than 100 m thick forms the remainder of the aquifer beneath and adjacent to the unconsolidated alluvium. Additional site details and sampling results were discussed in Puls and Barcelona (25).

During 1940-86, acidic mining waste solutions were discarded in an unlined lake formed behind waste and tailings piles. In 1986, pH at the lake surface was about 2.7 and the lake volume was about $5.5 \times 10^6\ \text{m}^3$. By May 1988, virtually all the lake water had been spread on inactive tailings piles to evaporate. Contamination of ground and surface waters in the area has been described by Eychaner (26).

In the alluvium, hydraulic conductivity is on the order of 200 m/d on the basis of cross-sectional area, hydraulic gradient, and measured outflow, whereas in the basin fill, estimated hydraulic conductivity is about 0.5 m/d.

Near the sampled wells, hydraulic conductivity was estimated on the basis of measured water-level declines and pumping rates during sampling periods using the solution of the unsteady ground-water flow equation (27). The estimates are within an order of magnitude at best, but are useful for comparisons among the wells because of the similarities in construction. The estimates range from 10 to 150 m/d for wells in the alluvium or uppermost basin fill. Estimated hydraulic conductivity for well 105, deeper in the basin fill, was 0.5 m/d. On the basis of hydraulic gradients that range from 0.005 to 0.008 and assumed porosity of 0.2 or 0.3, average ground-water flow velocities near the wells range from 0.02 to 3 m/d.

The second site studied is near Saco, Maine, about 30 km south of Portland and 7 km inland from the coast. This site was used for chromium waste disposal by a leather tannery from 1959 to 1977. Chromium wastes were dumped into 53 small unlined pits and two larger lagoons. The site geology consists of glacial

sediments, underlain by a sloping fractured bedrock surface. Sediment thickness ranges from 0 to 17 m. Glacial deposits consist of basal and ablation tills and glaciomarine sediments. The basal tills consist of gray, silty, fine to medium sands with gravel, coarse sand, cobbles, and boulders. Ablation till is less dense and consists of brown, fine to medium sand with silt, and layers of coarse sand and gravel. Glaciomarine deposits consist of gray to olive clayey silts with thin lenses of sand. The bedrock consists of interbedded phyllites with quartz stringers and secondary pyrite mineralization. Analysis of ground-water flow is complicated by both the fractured nature of the bedrock and an apparent ground-water divide in the overburden. Upward gradients have been determined at some locations associated with ground-water discharge to surface drainages. Depth to water table ranges from 1 to 2 m below ground surface.

The third site is near Elizabeth City, North Carolina, about 100 km south of Norfolk, Virginia and 60 km inland from the Outer Banks of North Carolina. A chrome plating shop, in use for more than 30 years, has discharged acidic chromium wastes into the soils and aquifer immediately below the shop. The site geology consists of typical Atlantic coastal plain sediments characterized by complex and variable sequences of surficial sands, silts and clays. In the vicinity of the plating shop, the uppermost soils are fine sand to sandy loam, overlying a thin sandy clay layer at about 2 m, overlying sand and silty fine sands, with pockets of silt and clay. In some locations, a dense gray clay layer substitutes for the sandy clay at 2 m. Fine to medium sands dominate from 4 to 20 m. A dense gray clay unit persists at a depth of 20 m. This depth is slightly variable and dips gently from north to south. Ground-water flow is generally to the northeast, however in the immediate vicinity of the plating shop, flow appears to be directly toward the Pasquotank River about 60 m north of the shop. Ground-water flow is somewhat complicated due to wind tides. Depth to ground water is about 2 m. An estimated hydraulic conductivity value of 15 m/d was based on aquifer test data. An average ground-water flow velocity for the site has been estimated as low as 0.004 m/d (28).

INSTRUMENTATION AND METHODS

Ground water was collected from more than 30 wells at the three sites studied, which covered a range of pH, solute concentration, redox and hydraulic conductivity (Table 1).

TABLE 1. Ground-water quality parameters for the three sites.

Site:	Arizona	Maine	North Carolina
pH (units)	3.5-6.1	6.0-7.8	5.7-6.9
Sp. Cond. (μ S/cm)	3020-7070	80-1600	170-800
Temp. ($^{\circ}$ C)	18.0-19.0	14.0-18.0	18.0-20.0
Oxygen (mg/L)	0.01-0.39	0.20-1.60	0.03-2.1
Redox Pot. (v)	0.25-0.44	0.08-0.19	0.22-0.38
Hydr. Conduct. (m/d)	0.5-200	~ 12	~ 0.5
Colloids (mg/L)	0.1-20	0.5-22	0.1-2.0

The sampling set-up used at the Saco and Elizabeth City sites is depicted in Figure 1. This was similar to the arrangement used in Globe, where a laser light scattering instrument was used for tracking particle concentrations instead of a turbidimeter and a bladder or submersible pump was used instead of a peristaltic pump (25). For comparison, a bailer was used in addition to the peristaltic pump at Saco and at Elizabeth City (Table 2). A multiparameter instrument with flow-through cell was employed in all cases to monitor pH, temperature, specific conductance, redox, and dissolved oxygen during purging and sample collection. Sample collection was initiated when all parameters, including turbidity, reached steady-state. An inflatable packer was used with the bladder and low-rate submersible pumps to reduce necessary purge volumes at the Globe site.

Figure 2 for well MW101 at Saco is typical of the trends for parameter equilibration during purging. Specific conductance, pH and temperature (not shown) were the least sensitive parameters, attaining steady-state values rather rapidly. In addition to the more sensitive parameters, contaminant concentrations are also plotted in Figure 3 for well MW1 at Elizabeth City. Chromate concentrations were shown to follow trends similar to turbidity, redox, and dissolved oxygen, the most equilibration-sensitive parameters.

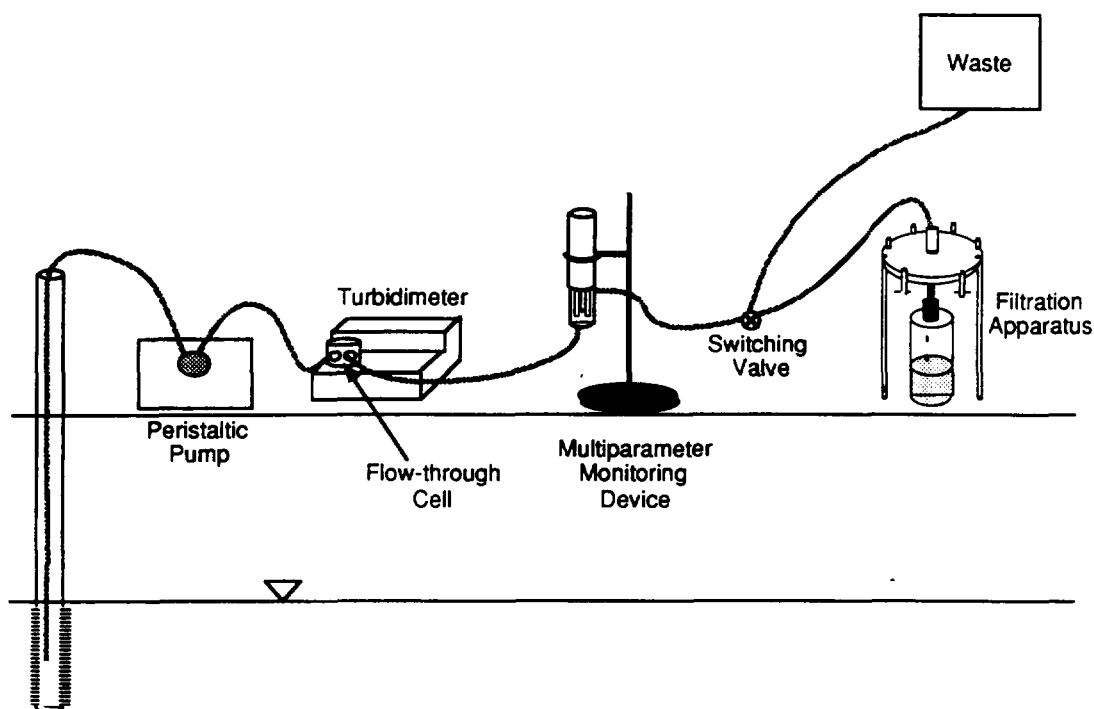


FIGURE 1. Sampling set-up for shallow wells (Saco, ME, and Elizabeth City, NC).

A Malvern Autosizer IIc was used at the Arizona site to measure suspended colloid size and concentrations. The effective size range measured was from 0.003 to 3 μm . The instrument determines the size distribution of suspended particles in this size range using laser light scattering techniques together with photon correlation spectroscopy. At the other two sites, suspended colloid concentrations were monitored with an in-line Hach turbidimeter. Turbidity is commonly measured in nephelometric turbidity units (NTU's). This is based on the comparison of the intensity of light scattered by a sample with the intensity of light scattered by a standard reference suspension under the same conditions.

TABLE 2. Pumps used in ground-water sampling.

Brand ¹	Type	Power Supply	Diameter (mm)	Discharge (L/min)
GeoTech	bladder	compressed air	44	0.6 - 1.1
"	peristaltic	12 V ac	-	0.2 - 0.3
Keck	submersible	12 V dc	44	2.8 - 3.8
Grundfos	submersible	240 V ac	95	12 - 92

¹ Use of brand names is for identification purposes only and does not imply endorsement by any agency of the United States Government.

Formazin polymer is used as the reference. Formazin has been found to be more reproducible than clay or natural water. Jackson candle units (JCU's) were previously used with candle turbidimeters, and kaolin was a standard reference material. Table 3 lists correlations between nephelometric turbidity units (NTU's), Jackson candle units (JTU's), and counts/1000/sec, as measured by two turbidimeters and a laser light scattering instrument respectively, using kaolinite as a common point of reference. Counts/1000/sec are photon counts recorded from laser light scattering measurements. The kaolinite used was a reference standard obtained from the Clay Minerals Repository at the University of Missouri.

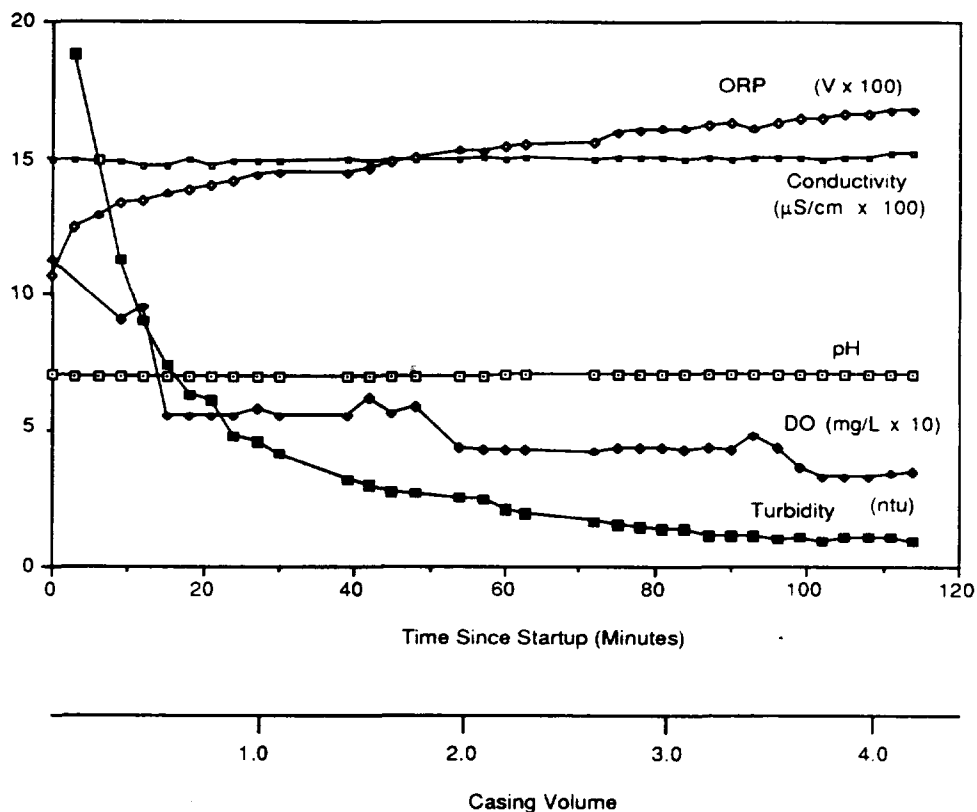


FIGURE 2. Equilibration of ground-water quality parameters during well purging (well MW101, Saco, ME, peristaltic pump at 0.2 L/min).

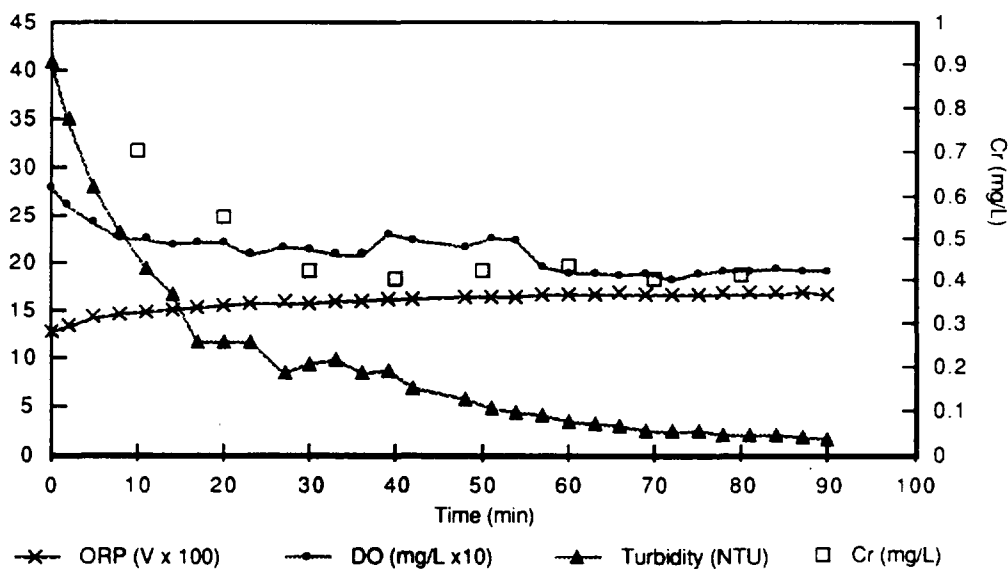


FIGURE 3. Equilibration of most sensitive ground-water quality parameters and chromate concentration during well purging (well 1, Elizabeth City, NC, peristaltic pump at 0.2 L/min).

Samples were collected both in air and under nitrogen at the Arizona site using a field glove box. Unfiltered and filtered samples were collected at all sites, the latter using 142-mm-diameter membrane filters ranging in pore size from 0.03 to 10.0 μm . Samples were acidified in the field, immediately after filtering, with double distilled concentrated nitric acid to $\text{pH} < 2$.

Elemental analyses were performed with inductively coupled plasma (ICP) for most elements; atomic absorption with graphite furnace (AAGF) for Cd, Pb, and As; and ion chromatography (IC) and a Technicon Autoanalyzer for major inorganic anions. Analytical precision on the ICP and AAGF were $\leq \pm 10$ percent, and on the IC and Technicon $\leq \pm 5$ percent. Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX) was used to identify colloidal material captured on the membrane filters.

Suspended Colloids and Sampling Devices

At the Globe, Arizona site, comparisons were made with respect to turbidity or suspended colloid concentrations and particle size distributions, using the bladder pump, the low speed submersible pump, and the high speed submersible pump. In well 105, over 13 times more particles were mobilized by the low speed submersible pump than by the bladder pump. This well is screened in the dense basin fill, where hydraulic conductivities are greater than two orders of magnitude lower than in the upper alluvium. Particles captured on filters were identified as iron coated albite, gypsum and calcite. This lower region of the aquifer is saturated with respect to calcite, but unsaturated with gypsum. Gypsum particles were not present in the bladder pump samples, but were present in the submersible pump samples, probably due to mixing of the upper and lower aquifer waters caused by the relatively high pump rate. Differences in water chemistry from the bladder pump and high-speed submersible pump samples in June, 1988, support this hypothesis (29). Interestingly, the calcite colloids in the bladder pump samples were uniformly spherical and approximately 1 μm in diameter.

In well 452, screened in the alluvium, over 20 times more particles were mobilized by the high speed submersible pump than by the bladder pump.

TABLE 3. Comparison of nephelometric turbidity units (NTU's), Jackson candle units (JCU's), photon counts from laser light scattering (cts/1000/sec) and kaolinite concentrations in water (mg/L).

NTU's	JCU's	cts/1000/sec	mg/L
0.2	-	2.3	0.1
2.7	3.0	20.5	1.0
12.2	7.0	77.7	5.0
25.2	10.0	175.9	10.0
63.0	28.5	438.2	25.0
121.0	53.0	699.8	50.0
227.0	100.0	1412.2	100.0

Mobilized particles captured on 0.1 μm filters were identified with SEM-EDX as predominantly smectite clays. Their presence was probably because well 452 is screened in relatively fine grained sediment in the alluvium, and is near the leading edge of the acidic waste plume where pH is decreasing rapidly and iron oxide coatings on colloidal clay are dissolving.

In well 503, also in the upper alluvium, successive use of the bladder, the low speed submersible, and the high speed submersible pumps produced increasingly more and larger particles in suspension. The two low-discharge pumps produced monomodal distributions of approximately 0.5 μm size particles. The highest discharge produced larger and slightly increased numbers of particles in a bimodal distribution centered around 800 and 2000 nm because of increased turbulence (Figure 4a-c). The predominant mineral identified on the filters from well 503 was gypsum. The upper alluvial aquifer is generally supersaturated with respect to gypsum due to dissolution of calcite by sulfuric acid disposed into the tailings ponds and leached into the subsurface for over 80 years.

Particles brought to the surface, even with the bladder pump, were as large as 10 μm . These were probably too large to be naturally suspended in situ, but there were clearly significant differences in particle population and size among the three different pumps. Increasing pump rate generally resulted in

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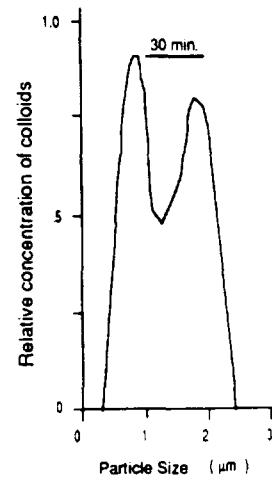
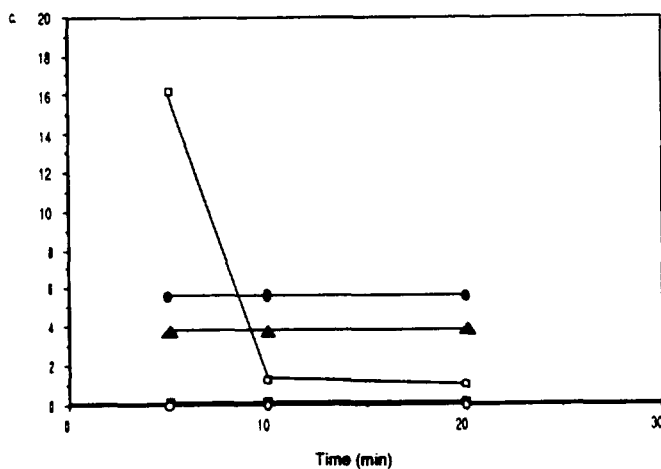
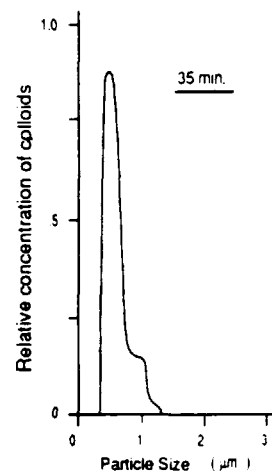
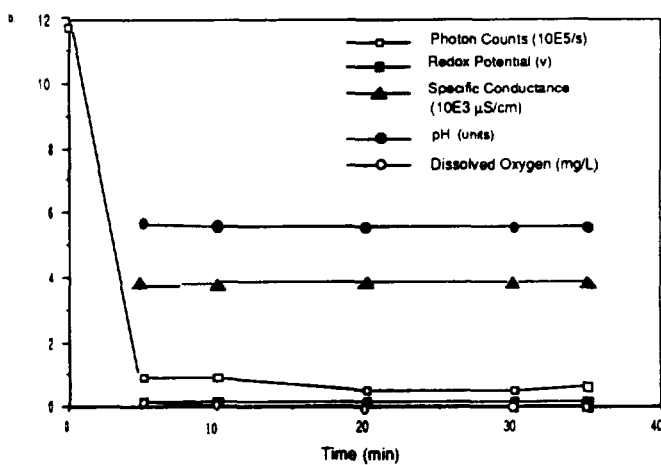
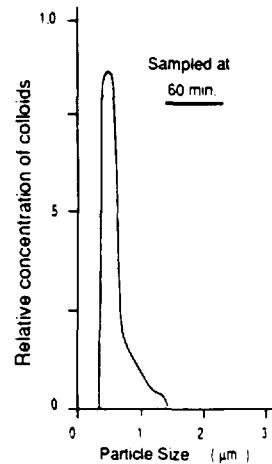
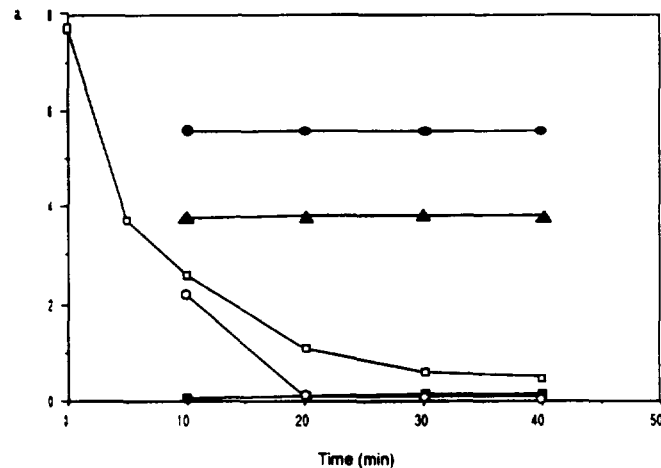


FIGURE 4 a-c. Changes in ground-water quality parameters and suspended particle size during well purging (well 503, Globe, AZ: [a] bladder pump; [b] low speed submersible pump; [c] high speed submersible pump).

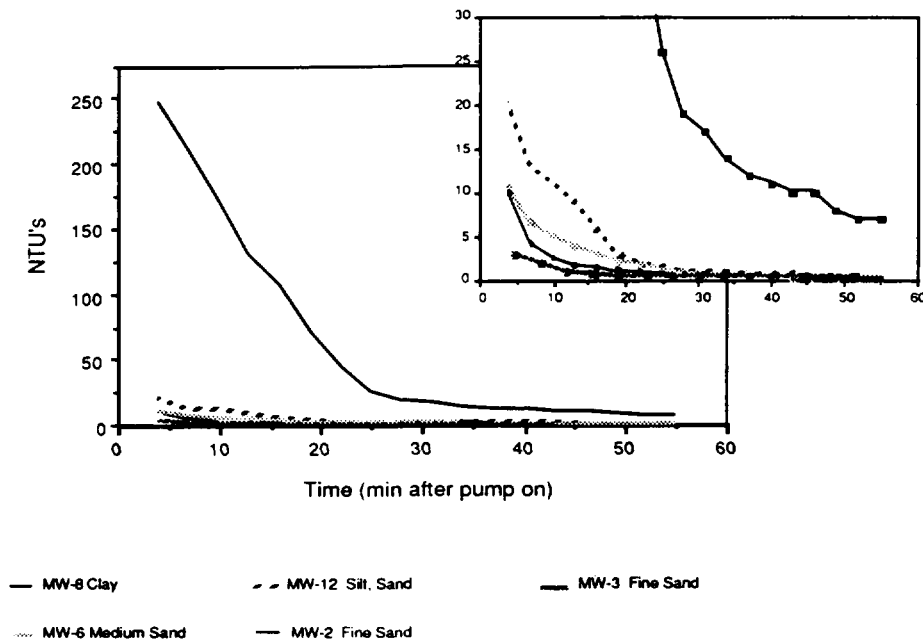


FIGURE 5. Equilibration of turbidity levels during well purging for several wells at the Elizabeth City site (peristaltic pump at 0.2 L/min).

increased turbidity and larger particles brought into suspension. Some anomalous behavior in this regard was caused by the sequence of pumps used for comparison in a given well (25).

A peristaltic pump was used at both the Saco, Maine and Elizabeth City sites because of the shallow depth to ground water, making lower pumping rates possible (0.2-0.3 L/min). At Saco, the turbidity of most wells equilibrated at less than 5 NTU's, however two wells equilibrated at 10 and 58 NTU's. The latter was an older well at the site and age or improper installation may explain the high turbidity value. At Elizabeth City, only 1 out of 12 wells equilibrated at more than 5 NTU's. This was well 8, the only well located (screened) in a clayey zone at the site (Figure 5).

A down-hole camera was used at the site during purging and sampling to evaluate the disturbance caused by emplacement and pumping. The peristaltic pump tubing was attached directly to the camera apparatus (similar in size and shape to a 2 in submersible pump), with the tubing inlet adjacent to the camera field-of-view. Pumping at about 0.2 L/min, significant disturbance was observed following camera emplacement, with a gradual decrease in colloidal density with time. Only minor increases in turbidity or colloidal density were observed when the peristaltic pump was turned on after both the pump tubing and the camera had been left in the screened interval overnight. Emplacement of the camera itself created the greatest turbidity and required overnight reequilibration in the absence of pumping to achieve steady-state colloidal density conditions in the screened interval. This was corroborated with turbidity measurements. Insertion of the peristaltic pump tubing and overnight equilibration prior to pumping produced approximately the same result, in terms of turbidity, as purging at low flow rate immediately upon insertion of the pump tubing (Figure 6). Disturbance, in terms of turbidity was directly related to the size of the sampling device inserted in the well (i.e. peristaltic pump tubing, down-hole camera, bladder pump). These observations argue strongly for dedicated sampling equipment as the optimal and perhaps most efficient manner of representative ground-water sample collection.

Filtration and Sampling Devices

Filtration differences among the different sampling devices used at the Arizona site were generally not significant. Greater than 10% differences for some elements were observed in only three wells, and were in samples collected with the high speed submersible pump. These differences were attributed to artifacts of excessive turbidity created down-hole by the pump compared to the natural hydrogeological conditions. Table 4 illustrates the observed differences due to the high speed submersible pump.

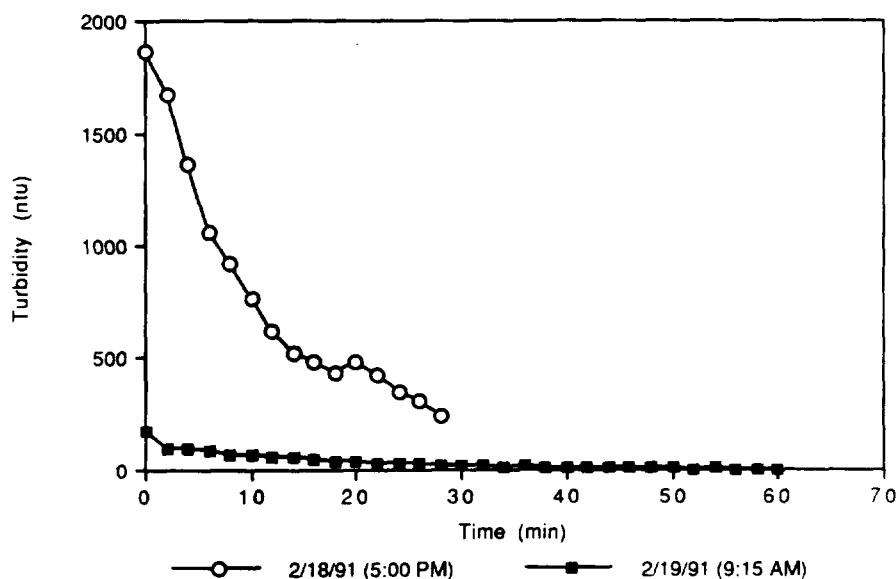


FIGURE 6. Comparison of turbidity equilibrations for well 8 (Elizabeth City, NC) using the peristaltic pump at 0.2 L/min immediately upon insertion of pump tubing (2/18/91) and following overnight (passive) equilibration (2/19/91).

Figure 7 shows chromium levels in samples from well 1 at Elizabeth City where samples were collected both with a peristaltic pump (0.2 L/min) and with a bailer.

The purge time for water quality parameter equilibration using the peristaltic was 1.3 hr or about two casing volumes. Bailed samples were collected after a standard three volumes had been purged. There were no significant differences in chromium concentrations between unfiltered, 5.0, 0.4 and 0.1 μm filtered samples, with the peristaltic pump. Not only were the bailed samples significantly different, but they were also 2 to 3 times higher than the peristaltic values. A similar response was observed in well 8 at the site. In all twelve wells, when the samples were collected with the peristaltic using a low pumping rate (~ 0.2 L/min) and the set-up depicted in Figure 1, there were no consistent differences observed in metal concentrations over the range from unfiltered to 0.1 μm -filtered.

Although the Saco site is a chrome tannery waste disposal site, the element of most interest in the ground water is arsenic. It is unclear at this time whether the elevated arsenic levels are naturally occurring or due to contamination. This is under further investigation since no historic data is available. Data from well 113 A (Figure 8) shows arsenic levels for samples collected using a peristaltic pump and a bailer. Similar results were observed in all wells with elevated arsenic at the site. Results are similar to those for chromium at Elizabeth City. Once again, there were consistently no differences observed in metal

TABLE 4. Cation concentrations, in mg/L, for well 51 using different filters (June 1988, 24 L/min, sampled in air).

Element	0.1 μm	0.4 μm	10 μm
Ca	383	385	417
Mg	313	317	343
K	7.0	7.5	10.3
Fe	2626	2662	2487
Mn	37.7	40.8	45.5
Al	214	222	251
Co	1.49	1.49	1.60
Ni	2.49	2.52	2.76
Zn	19.4	19.7	20.6

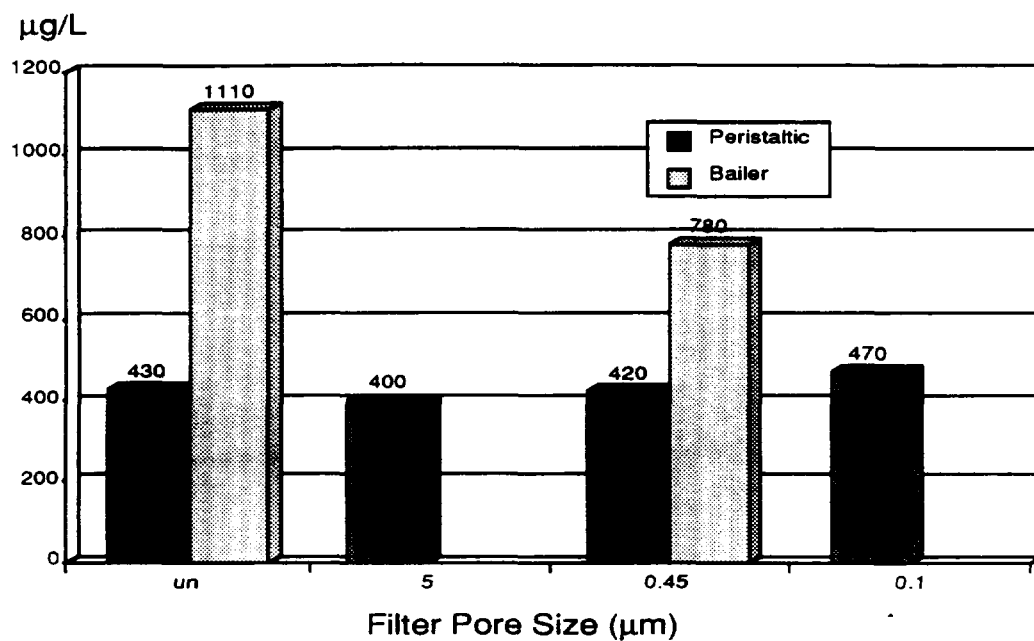


FIGURE 7. Differences in chromate concentrations for samples collected with peristaltic pump and bailer (well 1, Elizabeth City, NC).

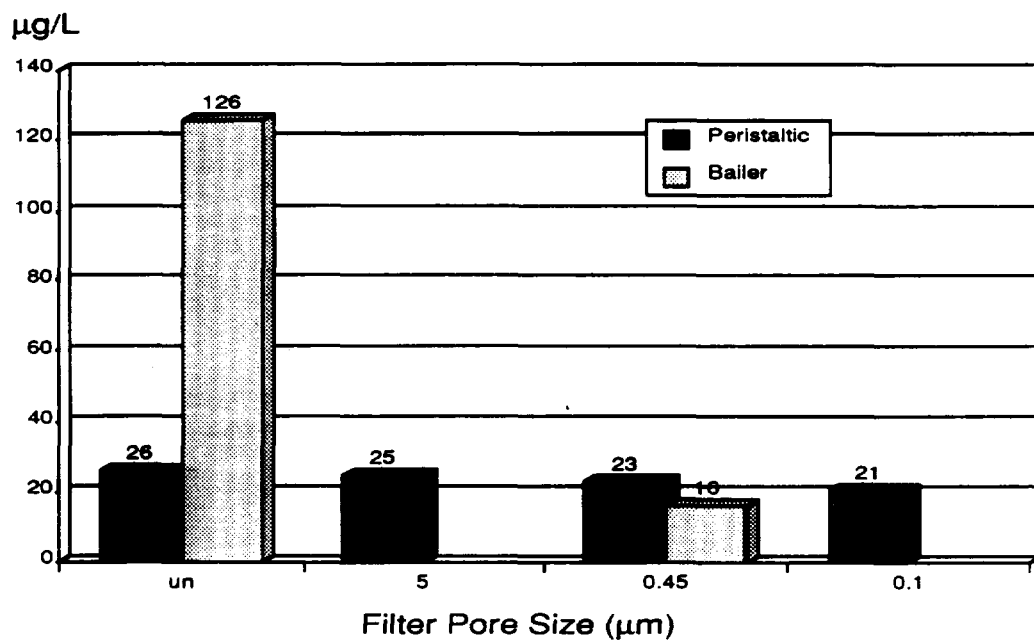


FIGURE 8. Differences in arsenic concentrations for samples collected with peristaltic pump and bailer (well 113A, Saco, ME).

concentrations using different filter pore sizes, but large differences were observed for filtered and unfiltered bailed samples and these two sets of values were generally different from the peristaltic pump sampled values. The sampling set-up used with the peristaltic pump (Figure 1) consistently produced the most reproducible results and provides increased confidence that these samples are more representative than those collected with the bailer.

Bailers are commonly used for both purging and sampling in small diameter, shallow wells, because of their convenience and low cost. Most bailers draw in water immediately upon contact with water in the well casing. If the sampling zone or screened interval is any significant distance from this point, even more importance is placed upon adequate well purging prior to sample collection. However, this is almost impossible from the standpoint of obtaining representative turbidity and dissolved oxygen values. Repeated insertion and withdrawal of the bailer causes significant surging, mixing and aeration, even when operated carefully. In addition, any results obtained with the bailer are extremely operator-dependant and therefore quite variable. Equilibrated turbidity values at the Elizabeth City site with the peristaltic pump were generally less than 2 NTU's, while with the bailer they were greater than 200 NTU's. At the Saco site, peristaltic pump turbidity values were generally less than 5 NTU's, but with the bailers ranged from 5 to greater than 200 NTU's.

It was interesting to note that there seems to be no significant contribution to contaminant transport from suspended and mobile colloids greater than $0.1\ \mu\text{m}$ at either the Elizabeth City or the Saco sites. However, this is not to say that colloidal facilitated transport by smaller particles may not occur at these sites.

Oxidation and Sampling

Oxidation of samples during sample collection, filtration, and preservation was assessed at the Pinal Creek, Arizona, site. Substantial differences were found for most wells between samples collected under nitrogen or in air. Work by Holm et al. (30) showed that diffusion of atmospheric gases through pump tubing can introduce measurable concentrations of oxygen into waters initially low in dissolved oxygen. This source of possible contamination for both sets of samples was minimized by collection of samples adjacent to the wellhead. Samples collected in air were directly exposed to atmospheric gases during filtration and acidification procedures. Significant differences (>10 percent) were observed in many of the wells. Variations in differences from well to well may have been caused by a number of different factors including:

- ♦ slightly different exposure times to air, depending on water-table depth and duration of filtration and preservation,
- ♦ dissolved-oxygen level,
- ♦ redox potential (Eh), and
- ♦ dissolved iron concentration.

Large differences in oxygen concentrations were measured for well 303, where dissolved iron concentration was greater than 200 mg/L (Table 5). Differences similar to those for well 303 were also observed in wells 51, 104, and 403. In contrast, the differences were small for well 503, where the dissolved iron concentration was less than 0.1 mg/L.

Another indication of the extent of oxidative effects on sample integrity was reflected in Eh values determined by various methods for well 51. The field-measured Eh value using a Pt electrode was 0.43 V. A calculated Eh value, assuming equilibrium between Fe^{3+} and $\text{Fe}(\text{OH})_3$, was 0.57 V (31). In March 1989, Fe^{2+} and Fe_{total} for well 51 were determined within one week of sample collection; Fe^{3+} was computed by difference, and Eh was calculated from the ratio of Fe^{3+} to Fe^{2+} . The calculated Eh was 0.51 V for the sample collected and analyzed in a nitrogen atmosphere and 0.76 V for the sample collected in air. Samples collected in the glove box were transported in nitrogen-pressurized containers, and the determinations were performed in laboratory glove boxes also pressurized with nitrogen.

Several possible errors are associated with all these Eh evaluation methods. Lindberg and Runnells (32) showed that many field Eh measurements may not reflect true redox conditions in ground waters. However, in acidic waters such as these, field measurements using Pt electrodes may be valid (33). Values calculated from equilibrium constants rely on the assumption that $\text{Fe}(\text{OH})_3$ is the predominant solubility controlling phase. Samples collected under nitrogen may have received some exposure to oxygen during sample collection, processing, and analysis. The Fe^{3+} values for March 1989 were small differences between two large numbers and are uncertain. Irrespective of these and other limitations in estimating Eh,

the large difference observed between 0.76 V for the sample collected in air and the other Eh values for well 51 demonstrates the extent of oxidation that can occur if care is not taken to limit oxygen exposure during sample-collection activities in suboxic and anoxic environments.

TABLE 5. Cation concentrations, in mg/L, for samples collected in air and nitrogen under atmosphere (mg/L, 0.40- μ m filter, < 1 L/min).

Element	Well 303		Well 503	
	air	nitrogen	air	nitrogen
Fe	177	215	0.04	0.09
Mn	37.4	44.7	68.3	68.7
Cd	0.02	0.02	0.01	0.01
Co	0.69	0.82	0.01	0.02
Cu	15.5	18.6	0.01	0.04
Ni	0.70	0.84	0.47	0.48
Zn	2.53	3.11	0.21	0.30

CONCLUSIONS

The studies summarized herein were initiated because of concerns about the use of 0.45 μ m-filtration for collection of metals samples in ground waters and the potential exclusion of colloidal-associated contaminants. While there have been indications of this mechanism of contaminant transport, its significance remains a question. For the three sites studied, significant contaminant concentration differences due to filter pore size were invariably due to the manner in which the samples were collected, rather than from contributions due to transport of colloidal material greater than 0.1 μ m in ground water. Methods and instruments which created excessive turbidity invariably produced such differences. Following the recommendations from Puls and Barcelona (14) resulted in no differences in elemental concentrations due to filter pore size. Monitoring of ground-water quality parameters during well purging provides the best indicator of when to initiate sample collection. The most sensitive indicators were redox, dissolved oxygen and turbidity, and trends during purging were correlated with contaminant concentrations in some wells. Exclusion of atmospheric gases during sample collection and processing is recommended in suboxic and anoxic ground waters.

DISCLAIMER

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